# PICOSECOND OPTICAL GENERATION AND DETECTION OF PHONON WAVES IN a-$As_2Te_3$

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## ABSTRACT

Using the pump and probe technique we have observed oscillations of photoinduced transmission in thin films of a-$As_2Te_3$. The oscillations have periods of 70-240 ps, depending on sample thickness. We ascribe these to phonon propagation in the films. Thermal expansion and carrier deformation potentials are discussed as the origin of these waves. Their velocity in a-$As_2Te_3$ is measured to be $v = 1.6 \times 10^5$ cm/s. The effect on transmission of heating by the laser pulse is estimated and compared to experiment.

## INTRODUCTION

In this paper we report on oscillations in photoinduced transmission of a chalcogenide glass. The results are interpreted in terms of an acoustic excitation propagating in the sample. Since optical methods are used for generation and detection of the phonon wave, the time resolution is enormously improved over conventional ultrasonic techniques. Limited only by the length of the light pulses ($\sim$ 1 ps), phonon propagation and attenuation can be studied in thin films. This is desirable when either the attenuation is very large, or the material can only be prepared as a thin film.

We will explain the detection technique and discuss two possible generation mechanisms for stress in our samples. The effect of heating by the laser pulse is included in the analysis.

## EXPERIMENTAL

Light pulses with a photon energy of $\hbar\omega_x$ = 2 eV with a duration of 1 ps were produced by a passively modelocked dye laser at a repetition rate of 0.5 MHz. Each pulse contained an energy of $\sim$ 1 nJ. The pump and probe method was used to measure the time dependence of transmission and reflection changes up to 1.8 ns following excitation.[1] Both pump and probe beam were incident onto the film from the substrate side and focussed to a $\sim$ 40 $\mu$m diameter spot.

The samples were amorphous films of $As_2Te_3$ sputtered onto sapphire substrates. The films with thicknesses 470, 900 and 1200 Å were prepared at substrate temperature $\theta_s$ = 300K, and film 1600 Å thick was prepared at $\theta_s$ = 77K. The absorption depth of

0094-243X/84/1200102-08 $3.00 

the samples at 2 eV photon energy was $\zeta$ = 300 Å, the sample with $\theta_s$ = 77K was slightly less absorbing.

## RESULTS

The changes in transmission as a function of time delay between pump and probe are plotted in Fig. 1 for samples of four different thicknesses at room temperature. The photoinduced response can be regarded as a superposition of two components:

(1) A steplike decrease in transmission ($-\Delta T/T \simeq 3 \times 10^{-3}$) at zero time delay followed by a monotonic relaxation and

(2) a damped oscillation with an amplitude of $3 \times 10^{-5}$ to $3 \times 10^{-4}$ and a period that depends on the thickness of the sample.

The data in Fig. 2 show that only a sharp peak remains of response (1) at a sample temperature of 10K, while the oscillating part (2) remains the same within the experimental error.

The distinct dependencies of the two components on sample thickness and temperature will be shown to originate from two different processes in the material. The plot of oscillation period vs. sample thickness of Fig. 3 shows a linear relationship.

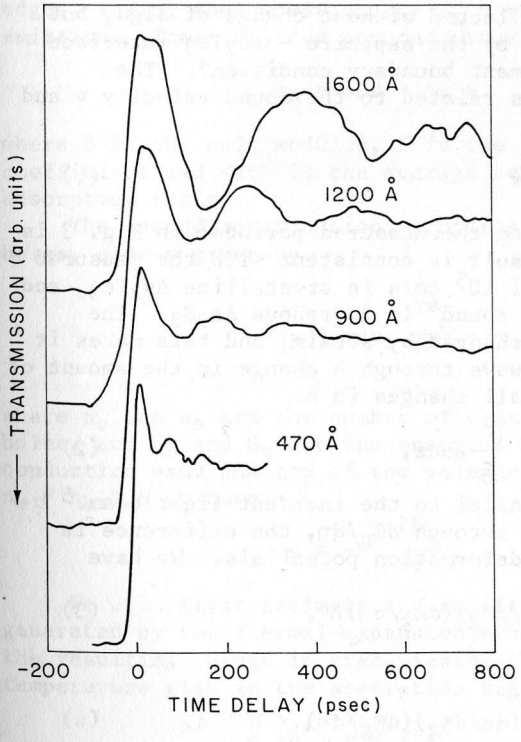


Fig. 1: Photo-induced transmission in a-$As_2Te_3$ at room temperature for films of various thicknesses.

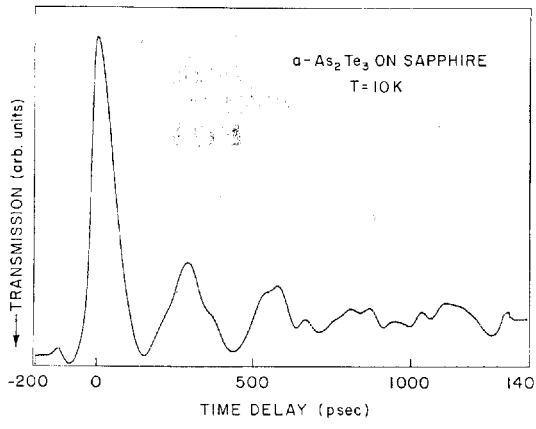


Fig. 2: Photoinduced transmission in a-$As_2Te_3$ at 10K of a film 1200 Å thick.

## INTERPRETATION

We begin by discussing response (2). We suggest that this oscillatory component of the signal results from a stress wave propagating in the sample. An elastic wave reverses its phase only at the free side of the film (zero stress boundary condition), whereas it is reflected without change of sign, but with a decrease in amplitude by the sapphire - $As_2Te_3$ interface (approximately zero displacement boundary condition). The oscillation period $\tau_o$ is thus related to the sound velocity v and the film thickness by:

$$\tau_o = 4d/v \qquad (1)$$

The velocity v determined from the measured periods[2] in Fig. 3 is $v = 1.6 \times 10^5$ cm/s. This result is consistent with the measured transverse sound velocity[3] of $10^5$ cm/s in crystalline $As_2Te_3$, and the velocity of longitudinal sound[4] in amorphous $As_2S_3$. The absorption coefficient $\alpha$ is changed by strain, and this makes it possible to detect a stress wave through a change in the amount of transmitted light T. For small changes in $\alpha$

$$\Delta T/T \simeq -\int_o^d \Delta\alpha dz, \qquad (2)$$

where the z direction is parallel to the incident light beam.[5] $\alpha$ is modulated by the strain $\eta$ through $dE_g/d\eta$, the difference in valence and conduction band deformation potentials. We have

$$\Delta\alpha = (d\alpha/dE_g)(dE_g/d\eta)\eta\ , \qquad (3)$$

so that

$$\Delta T/T = -(d\alpha/dE_g)(dE_g/d\eta) < \eta > d, \qquad (4)$$

where $<\eta>$ is the average strain in the sample. An oscillating

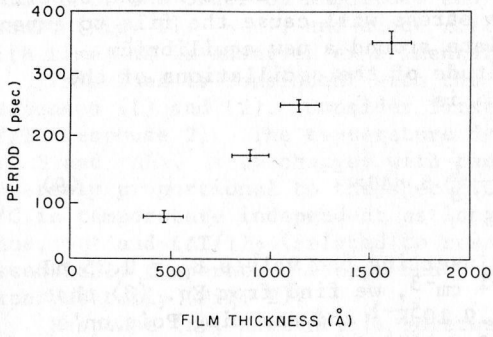


Fig. 3: Oscillation period vs. film thickness at room temperature.

change in transmission can thus result from an oscillating average strain.

Consider now the ways in which a stress wave can be generated through the laser pulse. We consider here two distinct mechanisms, both of which may play a significant role in the generation mechanism. The laser pulse creates a number of electron-hole pairs equal to the number N of absorbed photons. These will relax quickly (within a few picoseconds) to the band edges, losing the excess energy $E_x = (\hbar\omega - E_g)\ N$ by phonon emission. These emitted phonons produce a stress

$$\sigma_A = 3\beta B < \Delta\theta > \tag{5}$$

where B is the bulk modulus, $\beta$ is the linear thermal expansion coefficient and $<\Delta\theta>$ is the average temperature rise in the absorption region.

The second contribution $\sigma_B$ arises from the electrons and holes, and is given by

$$\sigma_B = -\left(n_e \frac{\partial E_c}{\partial \eta} - n_h \frac{\partial E_v}{\partial \eta}\right) \tag{6}$$

where $n_e$ and $n_h$ are the number of densities of electrons and holes, and $E_c$ and $E_v$ are the energies at the bottom of the conduction band and top of the valence band respectively. Since $n_e = n_h = N$ we have

$$\sigma_B = -N \frac{\partial E_g}{\partial \eta} \tag{7}$$

We will first estimate the amplitude of the stress wave generated by the thermal expansion stress $\sigma_A$, and the magnitude of the resulting change in transmission $\Delta T/T$. The average temperature rise in the absorption region is

$$< \Delta\theta > = E_x/\zeta AC \tag{8}$$

where A is the area of the illuminated spot, and C is the specific heat of the film. The sudden stress will cause the film to expand in the z-direction and oscillate around a new equilibrium thickness. The initial amplitude of the oscillations of the average strain in the film $\langle\eta\rangle$ is

$$\langle\eta\rangle_o = \frac{1+\nu}{1-\nu}\,\frac{\zeta}{d}\,\beta\,\langle\Delta\theta\rangle \qquad (9)$$

where $\nu$ is Poisson's ratio. Inserting the values $E_x = 0.35$ nJ, $A = 2 \times 10^{-5}$ cm$^2$, $C = 1.5$ JK$^{-1}$ cm$^{-3}$, we find from Eq. (8) that $\langle\Delta\theta\rangle = 4$K. Then using[6] $\beta = 1.9\ 10^5$K$^{-1}$ and assuming Poisson's ratio of 0.3 we find $\langle\nu\rangle = 1.3 \times 10^{-4}$ for 470 Å sample. Together with $d\alpha/dE_g = -3.5 \times 10^5$ cm$^{-1}$ eV$^{-1}$, estimated from an absorption edge measurement, and a deformation potential of $dE_g/d\eta = 2.3$ eV[7] we find from Eq. (4) $\Delta T/T \simeq 3 \times 10^{-4}$. Both the absolute value and the initial direction of the oscillations are predicted correctly by this, so that thermal expansion is clearly a possible origin for the oscillations.

Consider now the stress $\sigma_B$ due to the electrons and holes. We have calculated that this is numerically the same order of magnitude as $\sigma_A$. This term predicts the opposite sign of $\Delta T/T$ for the oscillations, which is apparently not in agreement with experiment. We have to be careful about this argument, however. To estimate the changes in absorption from $\Delta T/T$ we should correct for the effect of changes in reflectivity $\Delta R/R$. We have found that $\Delta R/R$ also contains an oscillatory component, which is of a magnitude comparable to $\Delta T/T$. Thus, it is conceivable that the phase of the absorption oscillations is not the same as is the phase of the oscillations of $\Delta T/T$. We are currently investigating this.

We now consider the origin of response (1). We propose that this comes from the change of the gap and the absorption coefficient due to the temperature rise in the film. One can divide $(\partial E_g/\partial\theta)_P$ (P = pressure) as follows:

$$\left(\frac{\partial E_g}{\partial\theta}\right)_P = \left(\frac{\partial E_g}{\partial\theta}\right)_V + 3\beta\left(\frac{\partial E_g}{\partial V}\right)_\theta \qquad (10)$$

In chalcogenide glasses[7] the thermal expansion term (second term) is known to be small compared to the thermal term $(\partial E_g/\Delta\theta)_V$. If we keep just the first term $\Delta T/T$ is

$$\frac{\Delta T}{T} = -\left(\frac{d\alpha}{dE_g}\right)\left(\frac{\partial E_g}{\partial\theta}\right)_V \zeta\,\langle\Delta\theta\rangle\ . \qquad (11)$$

For $(\partial E_g/\partial\theta)_V$ we use the value[7] for $As_2S_3$, and obtain

$$\Delta T/T \simeq -\,6 \times 10^{-3}. \qquad (12)$$

This is of the order of magnitude and sign of the experimental result (Fig. 1). $\langle\Delta\theta\rangle$, and hence $\Delta T/T$, should decay monotonically with time, as is observed experimentally.

This idea is consistent with the temperature dependence of responses (1) and (2). Consider first the oscillatory part of $\Delta T/T$ (response 2). The temperature dependent factors in Eq. (9) are $\beta$ and $\langle\Delta\theta\rangle$. $\langle\Delta\theta\rangle$ changes with temperature because it is inversely proportional to the specific heat. However, the product $\beta/C$ is temperature independent as long as Gruneisen's law holds. Thus, $\langle\eta\rangle$ and $(\Delta T/T)_2$ (related to response (2)) will be essentially temperature independent, as is found to be true experimentally (Fig. 2).

Response (1), however, is governed by the temperature behaviour of $(\partial E_g/\partial\theta)_V/C$ in Eq. (11). The specific heat is proportional to $\theta^3$ for $\theta << \theta_D$, $\theta_D$ denoting the Debye temperature. An Einstein model has been fitted to the gap of several amorphous semiconductors[8], which would imply that $(\partial E_g/\partial\theta)_V$ decays faster than $\theta^3$, such that $(\Delta T/T)$ in Eq. (11) decreases with temperature. It has been suggested[9] that optical and short wavelength acoustical phonons dominate $(\partial E_g/\partial\theta)_V$, and these high energy modes are frozen out at $\theta << \theta_D$. Thus the small relative strength of response (1) at 10K is consistent with its origin in the intrinsic change of $\alpha$.

The remaining peak at 10K of zero time delay, which does not extrapolate back from the oscillation amplitude, we can at this point only speculate about. It is possible that we see either hot carrier thermalization or a decay of optical phonons into long wavelength acoustical phonons. Alternatively an unusually large thermal conductivity of the film at 10K could cause $\langle\Delta\theta\rangle$ of Eq. (9) to decay so rapidly.

Finally in Fig. 4 we show a computer simulation of a stress wave propagating through a 1000 Å film of $As_2Te_3$. Plotted in each figure is stress vs. distance in the film. The frames differ by 20 ps each. At t = 0 ps the exponential absorption of the light incident from the left determines the initial stress distribution. The wave then develops in time, and the amplitude is reduced by reflection losses at the sapphire-$As_2Te_3$ interface on the left. The experimentally measured quantity $(\Delta T/T)_2$ is proportional to the average strain shown in Eq. (4), which we plot in the bottom frame vs. time. It can be seen that response (2) is simulated rather well. Note that most of the damping of the wave occurs through reflection losses at the substrate interface, since the simulation assumes no attenuation in the film.

## SUMMARY

We have presented a novel method of optically generating and detecting phonon waves. We discussed two mechanisms that can produce the observed strain and show that heat can make a significant contribution to photoinduced transmission measurements if the excitation energy is sufficiently larger than the bandgap.

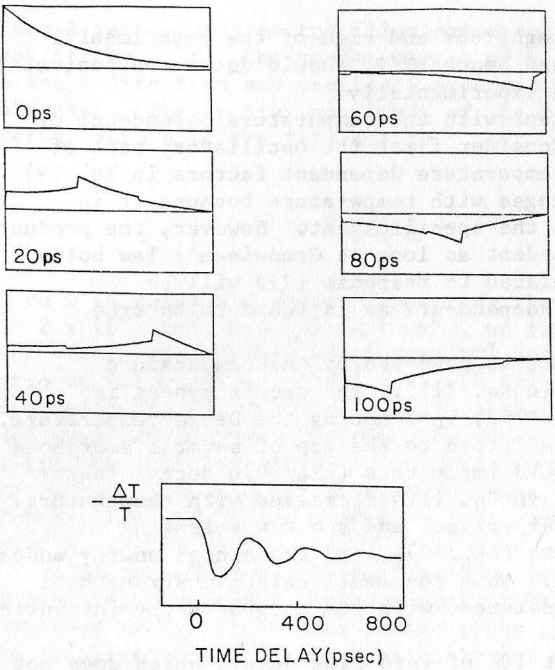


Fig. 4: Computer simulation of a propagating stress wave and of photo-induced transmission corresponding to response (2) (see text).

The phonon generation mechanism is a tool for studying high frequency ($\sim$ 10 to 100 GHz) phonon velocity and attenuation in thin films and highly attenuating materials on a very short time scale, when a-$As_2Te_3$ is used as a transducer.[12]

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1. E. P. Ippen and C. V. Shank, Ultrashort Light Pulses, edited by S. L. Shapiro (Springer, New York, 1977), p. 102 ff.

2. We do at the present time not understand why the plot does not extrapolate precisely through the origin.

3. G. Cibuzar and C. Elbaum, private communication.

4. D. Gerlich, E. Litor and O. L. Anderson, Phys. Rev. B20, 2529 (1979).

5. This treatment does not yet include changes in reflectivity of the two surfaces.

6. We have used the value for $As_{0.45}Te_{0.55}$ given by J. Cornet and J. Schneider, 4th International Conference on the Physics of Non-Crystalline Solids, edited by G. H. Frischat (Trans. Tech. Publications, Clausthal, 1976), p. 397.

7. J. M. Besson, J. Cernogora, and R. Zallen, Phys. Rev. B22, 3866 (1980).

8. G. O. Cody in Hydrogenerated Amorphous Silicon, ed. J. Pankove (Academic Press, 1984), Chapter 2, Vol. 21B, p. 11.

9. P. O. Persans, A. F. Ruppert, G. D. Cody and B. G. Brooks, to be published.

10. G. D. Cody, T. Tiedje, B. Abeles, B. Brooks and Y. Goldstein, Phys. Rev. Lett. 47, 1480 (1981).

11. Z. Vardeny, J. Strait and J. Tauc, Picosecond Phenomena III. ed. S. L. Shapiro (Springer Verlag, New York, 1982), p. 372.

12. C. Thomsen, J. Strait, Z. Vardeny, H. J. Maris, J. Tauc and J. J. Hauser, Phys. Rev. Lett., in press.